

Selective oxidation and direct decolorization of cationic dyes by persulfate without activation

Bing Yang, Qiuping Luo, Qinman Li, Yuan Meng, Li Lingli and Yucheng Liu

ABSTRACT

The aim of this work was to investigate the selective oxidation and direct decolorization of selected organic dyes (Methylene Blue (MB), Rhodamine B (RhB) and Orange II (OrgII)) by persulfate (PDS) without activation. Results show that the decolorization rate of MB was up to 58.0% within 10 minutes, while those of RhB and OrgII were only about 29.6% and 3.0% after 80 minutes, respectively. In comparison with the negligible impacts of pH from 2.0 to 9.0 on MB and OrgII decolorization, RhB decolorization rate obviously varied with the pH changes, and acid pH condition was beneficial for RhB decolorization. Quenching tests implied that the decolorization of dyes by PDS without activation was a nonradical oxidation process rather than sulfate radical oxidation. A plausible mechanism is that the decolorization process is attributed to the charged states of the dyes at different pH conditions, and thus direct electron transfer from dyes to PDS may occur, which is responsible for the bleaching of dyes. This study points out the potential bleaching capability of PDS without activation on cationic dyes, which may have important implications for selective oxidation treatment of dye wastewater.

Key words | cationic dyes, direct decolorization, nonradical oxidation, peroxydisulfate

Bing Yang (corresponding author)

Qiuping Luo

Qinman Li

Yuan Meng

Li Lingli

Yucheng Liu

School of Chemistry and Chemical Engineering,

Southwest Petroleum University,

Chengdu 610500, Sichuan,

China

E-mail: yangb2016@swpu.edu.cn

Bing Yang

Li Lingli

Yucheng Liu

Research Institute of Industrial Hazardous Waste

Disposal and Resource Utilization,

Southwest Petroleum University,

Chengdu 610500, Sichuan,

China

HIGHLIGHTS

- Persulfate selectively and effectively decolorized cationic dyes or dyes with positive charges under certain pH conditions.
- Direct and non-radical oxidation process was proposed for decolorization of Methylene Blue and Rhodamine B by persulfate without activation.
- Direct decolorization of dyes by persulfate without activation was not complete, and the degradation of dyes was limited.

INTRODUCTION

Peroxydisulfate (PDS) has been widely utilized as a bulk oxidant in advanced oxidation processes (AOPs) for removing organic pollutants in water and soil (Waclawek *et al.* 2017; Zhou *et al.* 2019). Generally, PDS is activated to produce sulfate radical ($\text{SO}_4^{\cdot-}$) as the highly reactive oxidant species (ROS) to oxidize organic compounds almost non-selectively

(Neta *et al.* 1988). Activation of PDS to produce $\text{SO}_4^{\cdot-}$ requires the input of energy (such as heat, ultraviolet light, and ultrasound), or low-valent transition-metal ions or oxides (Tan *et al.* 2012; Zarei *et al.* 2018; Wang *et al.* 2019).

AOPs based on $\text{SO}_4^{\cdot-}$ are capable of decomposing various refractory organic compounds in wastewater treatments (for instance, the decolorization and decontamination of wastewater from textile and dyeing industries (Yang *et al.* 2010; Li *et al.* 2016), treatment of pharmaceutical wastewater (Gao *et al.* 2019), and phenolic wastewater (Sun *et al.* 2012; Song *et al.* 2018). In the recent several

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY-NC-ND 4.0), which permits copying and redistribution for non-commercial purposes with no derivatives, provided the original work is properly cited (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

doi: 10.2166/wst.2021.177

years, non-radical pathways of activated PDS to oxidize organic pollutants in environmental remediation have also attracted attention. PDS activation without generation of SO_4^- but effective degradation of organic compounds was achieved via the coupled process of PDS with CuO (Zhang *et al.* 2014), porous carbon aerogel (Jiang *et al.* 2018), sludge-derived biochar (Yu *et al.* 2019), cubic mesoporous carbons (Duan *et al.* 2018b), or carbon nanotubes (Lee *et al.* 2015). The non-radical pathway of activated PDS was proposed to oxidize target pollutants via direct electron transfer from organics to PDS, facilitated by the above catalysts or producing singlet oxygen as reactive oxidative species (ROS) (Zhu *et al.* 2019). Compared to SO_4^- pathways, the non-radical processes of PDS oxidation towards organics were more selective and showed significant advantages by achieving much higher degradation capacity and avoiding the formation of highly chlorinated degradation products in the presence of chloride ions (Duan *et al.* 2018a).

While both the radical and non-radical processes of PDS with activation for AOPs have been well studied, there is little information on the direct oxidation of PDS itself without activation to degrade organic pollutants in water, even though PDS is actually a strong oxidant ($E_0 = +2.01$ V) (Shih *et al.* 2013). However, peroxymonosulfate (PMS, HSO_5^- , $E_0 = +1.82$ V), as another kind of persulfate, has been proved to be capable of decomposing some organic compounds (amino acids (Ruiz *et al.* 2019), antibiotics, pharmaceuticals, phenolics (Yang *et al.* 2018), cationic dyes (Lei *et al.* 2016)) by direct reaction with PMS without activation.

Therefore, the direct reaction of PDS towards certain organic pollutants should be theoretically feasible due to its relatively high redox potential.

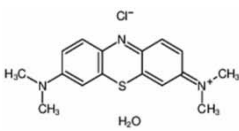
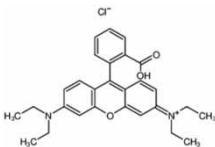
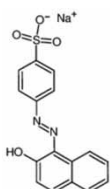
In this present study, we focus on the unactivated PDS in water to decolorize several azo dyes, and the decolorization kinetics and the reaction mechanism were investigated. We assumed that the direct reaction between azo dyes and PDS should be related to the charged state of dyes under various pH conditions, since the PDS ion ($\text{S}_2\text{O}_8^{2-}$) carries two negative charges. Thus, three dyes (Rhodamine B (RhB), Methylene Blue (MB) and Orange II (OrgII)) with different charged states as shown in Table 1 under our experimental conditions were selected for detailed mechanistic investigation. The effects of pH, PDS dosage, ROS scavengers and ferrous ion on decolorization rates were studied. We found that PDS without activation can effectively decolorize dyes and in deed depends on the charged states of dyes. This study represents the first example, to our knowledge, demonstrating the oxidation of dyes by unactivated PDS alone and associating the reaction rate with the charged states of pollutants.

MATERIALS AND METHODS

Materials

Methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}\cdot 3\text{H}_2\text{O}$, $\geq 98.5\%$), sodium persulfate (PDS, $\text{Na}_2\text{S}_2\text{O}_8$, $\geq 98.0\%$), Rhodamine B (RhB),

Table 1 | The parameters of three dyes

Dye	Molecular formula	Structure	Ion with charges at different pH ^a
Methylene blue (MB)	$\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$		1.86, pH 1.7 1.01, pH 4.6 1.00, pH 6.5 1.00, pH 8.0
Rhodamine B (RhB)	$\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_5$		1.98, pH 1.7 0.43, pH 4.6 0.01, pH 6.5 0.00, pH 8.0
Orange II (OrgII)	$\text{C}_{16}\text{H}_{11}\text{N}_2\text{NaO}_4\text{S}$		-1.00, pH 1.7 -1.00, pH 4.6 -1.00, pH 6.5 -1.00, pH 8.0

^aThe specific parameters of the three dyes calculated from chemicalize.org by ChemAxon (Swain 2012).

$C_{28}H_{31}ClN_2O_3$, $\geq 98.0\%$), Orange II (OrgII, $C_{16}H_{11}N_2NaO_4S$, $\geq 86.0\%$), Ethanol (C_2H_6O , $\geq 99.5\%$), 2-methyl-2-Propanol ($C_4H_{10}O$, $\geq 99.0\%$), 1,4-Benzoquinone ($C_6H_4O_2$, $\geq 98.5\%$), and Iron(II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, 99.0.0%–101.0%) were purchased from Kelong Chemical Co, Ltd (Chengdu, China). All reagents were of analytical grade and used without further purification. All solutions were prepared in ultrapure water (resistivity $> 18.2 \text{ M}\Omega \cdot \text{cm}$).

Experimental procedure

The dye decolorization experiments were performed in a 1 L flask with three necks at a room temperature ($25 \pm 2^\circ \text{C}$). Each run was performed in duplicate or triplicate, and the average values were adopted to ensure reproducibility. The three dyes (MB, RhB, and OrgII) were used at different initial concentrations of MB at 25 mg/L (RhB 20 mg/L, OrgII 35 mg/L) to give a close maximum absorbance around 1.60 at the respective characteristic wavelength. Dye solution and PDS stock solution were added into the flask, and the concentration of PDS was 50 times that of dyes at molar ratio, unless otherwise specified. The initial solution pH was adjusted with 0.1 M H_2SO_4 or 0.1 M NaOH (within ± 0.1 unit fluctuation). The exact experimental conditions are more clearly listed in the figure or table captions. At each given interval, the target reaction solution (2.5 mL) was withdrawn, and immediately determined the real-time absorbance using a UV-Vis spectrophotometer. To identify the active species formed in the PDS/dyes system, quenching tests with three scavengers (ethanol (EtOH), tert-butyl alcohol (TBA) and p-benzoquinone) as the quenching agents were conducted.

Analytical methods

The residual concentration of dyes was monitored at the appropriate λ_{max} using a UV-Vis spectrophotometer (UV-762, Shanghai Precision Scientific Instrument Co, Ltd). Total organic carbon (TOC) of water samples was detected by a TOC analyzer (Shimadzu, Japan). The pH of the solution was monitored by a pHs-3C meter (Rex, China).

The experimental data processing and drawing were mainly conducted by the software Office Excel 2016 and Origin 2017. The change of dye content was calculated by C_t/C_0 , where C_t represents the dye concentration at time t , and C_0 is the initial concentration

RESULTS AND DISCUSSION

Decolorization of different dyes by PDS

As shown in Figure 1, three dyes (MB, OrgII and RhB) were decolorized by PDS without activation by catalysts or energy input. Compared with the negligible decolorization of OrgII, about 58.0% of MB was bleached by PDS without activation within 10 minutes. Besides, only about 29.6% of RhB was decolorized after 80 minutes.

The different decolorization performances towards the three dyes by PDS without activation suggest that PDS has high selectivity towards certain dyes, like MB. This might be closely related to the charge carried by PDS and dyes. PDS dissociates to produce persulfate ion ($S_2O_8^{2-}$) with two negative charges. The charged states of dissociated organic dyes molecule are closely related to their molecule structures and the deprotonation functional groups (Wang & Zhu 2007). As shown in Table 1, with the pH values varying from 1.7 to 8.0, the dissociated MB molecule always carries positive charges, and the dissociated OrgII molecule carries one negative charge, while the dissociated RhB molecule carries the charges from positive to neutral as the pH values increase. MB can dissociate cations which is easy to combine with electronegative substances in aqueous solution (Vinuth et al. 2017). Therefore, the direct decolorization rate by PDS was fastest with cationic dye (MB) (Gao et al. 2016), and was slow with neutral dye (RhB), but was nearly zero with anionic dye (OrgII). Jiang et al. (2013) also observed a similar experimental phenomenon. The

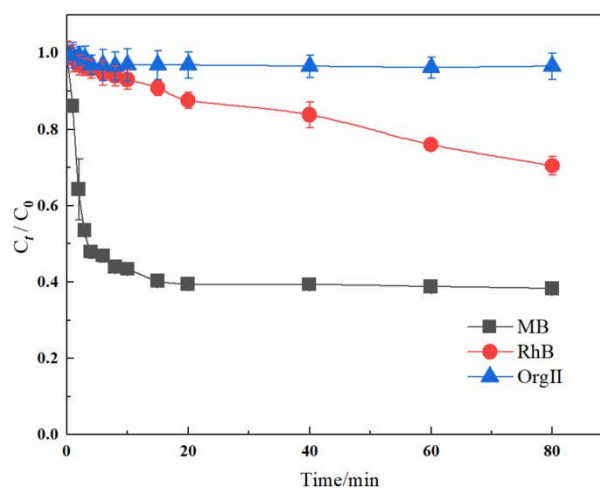


Figure 1 | Dye decolorization by PDS without catalyst addition. Condition: $[MB]_0 = 25 \text{ mg/L}$, $[RhB]_0 = 20 \text{ mg/L}$, $[OrgII]_0 = 35 \text{ mg/L}$, $n[PDS]_0 : n[MB]_0 (n[RhB]_0, n[OrgII]_0) = 50 : 1$, initial pH = 5.8 and temperature = $25 \pm 2^\circ \text{C}$.

mechanism of MB, RhB and Org II decolorization by PDS under different pH conditions were further studied.

Effects of initial pH on dyes decolorization by PDS

Considering the different charged states of MB, OrgII and RhB under different pH conditions from 1.7 to 8.0 (Table 1), the effects of initial pH at 2.0, 5.0, 7.0 and 9.0 on dyes decolorization by PDS were explored to verify whether the pH condition or the charged state of the dissociated dye molecule plays a more important role in dye decolorization. As shown in Figure 2(a) and 2(b), the MB and OrgII removal efficiency barely varied with the pH changes, and the decolorization rate of MB was more than 60% in 30 minutes. In addition, OrgII hardly reacts with PDS under different pH conditions, which is basically

consistent with the previous discussion. However, acidic pH condition was beneficial for the RhB decolorization, and the best removal efficiency (about 31.1%) was obtained at around acid pH (pH = 2.0) in 5 minutes (Figure 2(c)). Taken together, it is reasonable to believe that the charged states of dissociated dye molecules, which varies with pH condition, plays a vital role in dye decolorization by PDS without activation.

Quenching experiments for RhB decolorization

Ethanol (EtOH), Tert butyl alcohol (TBA), and p-benzoquinone were used as scavengers to verify that the dominant reactive oxidant species resulted in the decolorization of RhB in RhB/PDS system with pH at 2. TBA can effectively quench $\cdot\text{OH}$ rather than SO_4^- due to the faster reaction

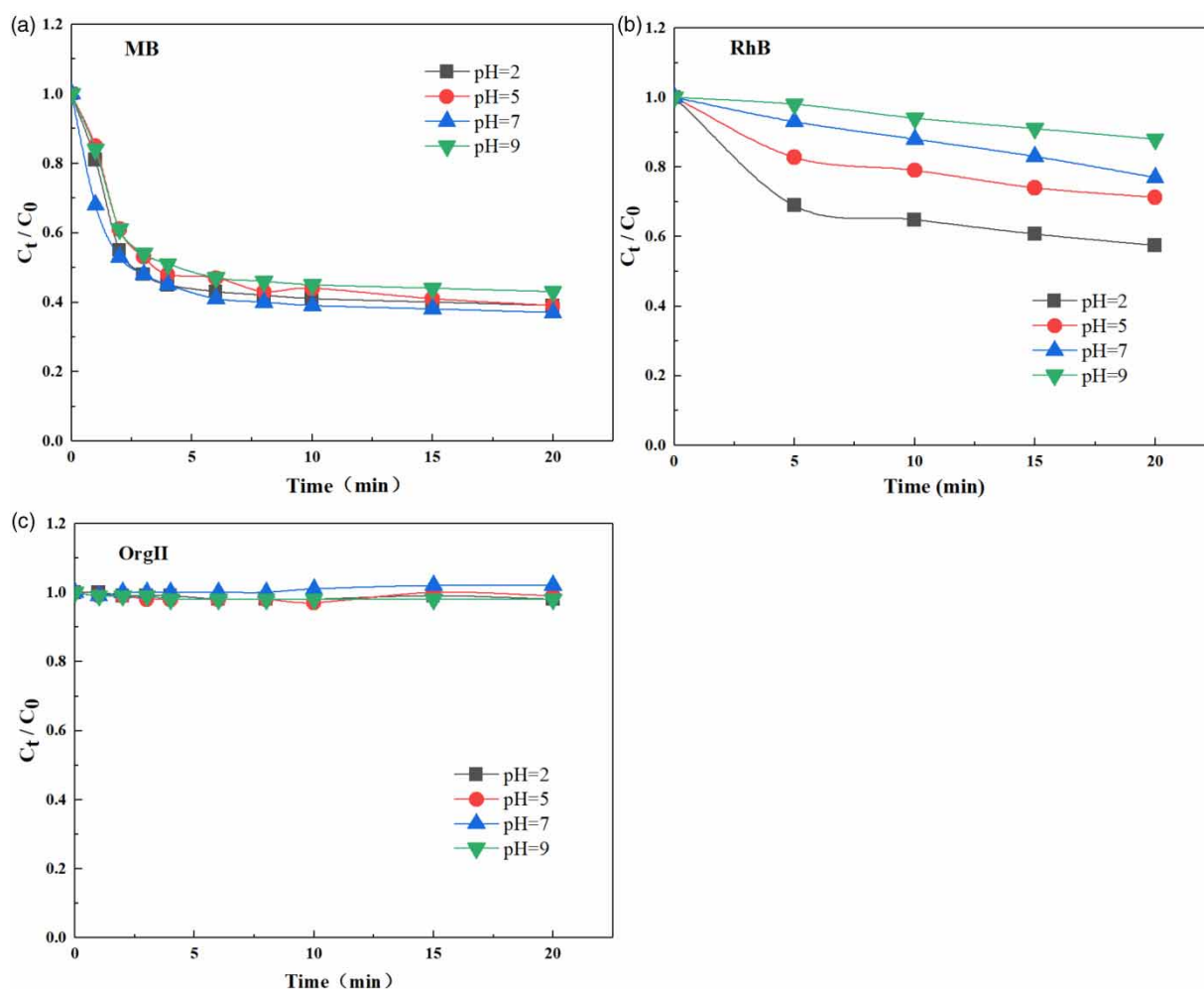


Figure 2 | Effects of initial pH on (a) MB, (b) RhB and (c) OrgII decolorization by PDS. Condition: $[\text{MB}]_0 = 25 \text{ mg/L}$, $[\text{RhB}]_0 = 20 \text{ mg/L}$, $[\text{OrgII}]_0 = 35 \text{ mg/L}$, $n[\text{PDS}]_0 : n[\text{MB}]_0$ ($n[\text{RhB}]_0$, or $n[\text{OrgII}]_0$) = 50 : 1, initial pH = 5.8 and temperature = $25 \pm 2^\circ\text{C}$.

constant between TBA and $\cdot\text{OH}$ ($K_{\text{TBA}+\cdot\text{OH}} = (3.8\text{--}7.6) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$) than that between TBA and $\text{SO}_4^{\cdot-}$ ($K_{\text{TBA}+\text{SO}_4^{\cdot-}} = (4.0\text{--}9.1) \times 10^5 \text{ M}^{-1}\text{s}^{-1}$) (Xu *et al.* 2016). However, EtOH can quench both $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ efficiently, since the reaction rate constant between EtOH and $\text{SO}_4^{\cdot-}$ ($K_{\text{EtOH}+\text{SO}_4^{\cdot-}} = (4.3\text{--}5.6) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$) is as high as that between EtOH and $\cdot\text{OH}$ ($K_{\text{EtOH}+\cdot\text{OH}} = 2.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Clifton & Huie 1989; Deister & Warneck 1990; Motohashi & Saito 1993). Therefore, in this study, TBA was used as a scavenger for $\cdot\text{OH}$, while EtOH was used as a scavenger of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$. In addition, p-benzoquinone was used as a scavenger for $\text{O}_2^{\cdot-}$ (Antonopoulou & Konstantinou 2014). And the addition of sodium sulfate was intended to inhibit the decolorization efficiency via the competition of $\text{SO}_4^{\cdot-}$ and $\text{S}_2\text{O}_8^{2-}$ to combine with RhB, since some parts of the molecular structures of $\text{SO}_4^{\cdot-}$ and $\text{S}_2\text{O}_8^{2-}$ are similar.

Decolorization of RhB and pseudo second-order reaction kinetics fitting are shown in Figure 3. In comparison with the control treatment, adding EtOH or TBA showed weak inhibition on RhB decolorization, indicating that $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ was not the dominant ROS contributing to RhB decolorization by PDS without activation. However, compared with TBA, EtOH presented a relatively higher inhibition effect on RhB decolorization, implying that a small part contribution from $\text{SO}_4^{\cdot-}$ in the oxidation process may be possible. There was almost no inhibition of p-benzoquinone treatment, suggesting that $\text{O}_2^{\cdot-}$ was absent from the reaction. In addition, the RhB decolorization rate in sodium sulfate treatment also decreased slightly, which partly supported the competitive combination of RhB with $\text{SO}_4^{\cdot-}$ and $\text{S}_2\text{O}_8^{2-}$. Considering the

different inhibition performance of EtOH, TBA, p-benzoquinone, and sodium sulfate on RhB decolorization, PDS direct oxidation via non-radical pathway was proposed to be the dominant process for RhB decolorization by PDS without activation, and there might be a small part contribution from $\text{SO}_4^{\cdot-}$.

Quenching experiments for MB decolorization

The similar quenching experiments as above were taken to verify the dominant ROS for MB decolorization by PDS with pH at 5.8. As seen in Figure 4, in the early stage of the reaction, TBA and p-benzoquinone treatments presented a relatively obvious inhibitory effect on MB decolorization, while EtOH and Na_2SO_4 treatments showed a little promoting effect on MB decolorization. Thus, the role of the sulfate radical or hydroxyl radical in MB decolorization by PDS can be excluded, since EtOH treatment did not inhibit MB decolorization. Furthermore, after 20 minutes of the reaction, MB decolorization rates were close (60%–70%) among the quenching treatments and the control treatment. Therefore, MB decolorization by PDS in this study was not significantly involved with free radicals or $\text{O}_2^{\cdot-}$, and the non-radical pathway by PDS direct oxidation may also be the main contribution for MB decolorization. A plausible mechanism was proposed that cationic dyes (i.e. MB^+) firstly form a complex with the $\text{S}_2\text{O}_8^{2-}$ ion, as Equation (1), due to the electrostatic attraction. Subsequently, direct electron transfer from cationic dyes to PDS, as Equation (2), may occur, and probably this is responsible for the bleaching of

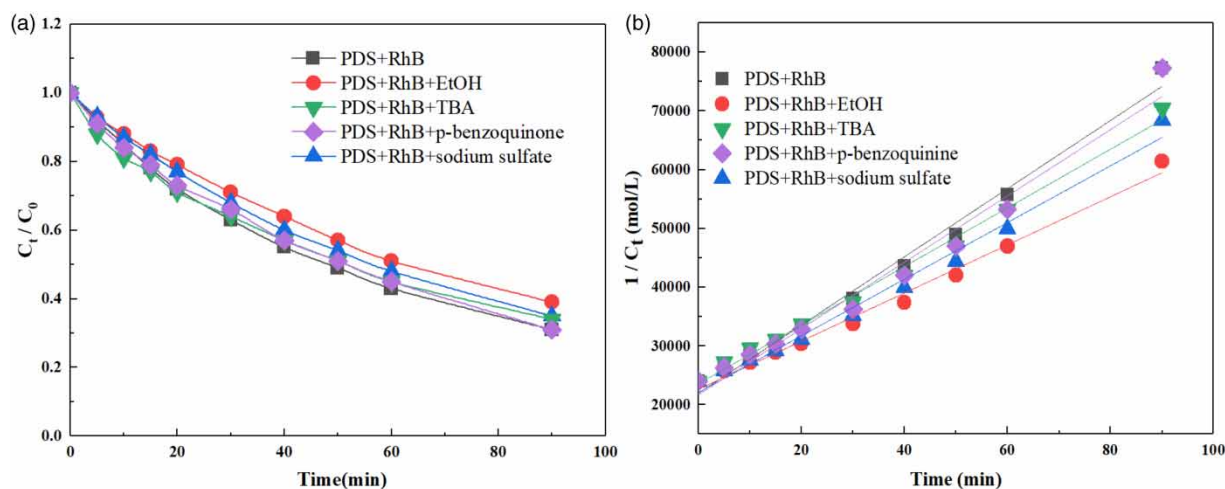


Figure 3 | (a) Influence of different quenching agents on RhB decolorization by PDS at pH = 2. (b) Second-order reaction kinetics fitting of quenching reaction. Condition: $[\text{RhB}]_0 = 20 \text{ mg/L}$, $n[\text{PDS}]_0 : n[\text{Sodium sulfate}] : n[\text{RhB}]_0 = 50 : 50 : 1$, $[\text{EtOH}]_0 = 7.85 \text{ g/L}$, $[\text{TBA}]_0 = 7.9 \text{ g/L}$, $[\text{p-benzoquinone}]_0 = 1.0 \text{ g/L}$, initial pH = 2 and temperature = $25 \pm 2 \text{ }^\circ\text{C}$.

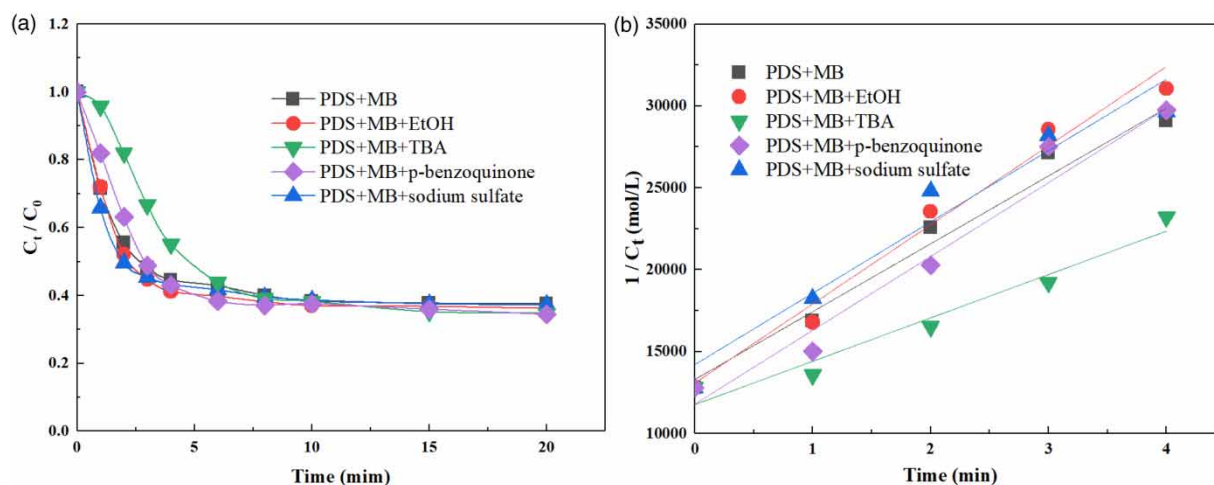
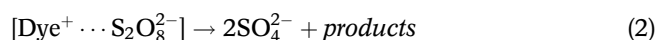
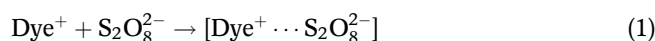


Figure 4 | (a) Influence of different quenching agents on MB decolorization by PDS at pH = 2. (b) Second-order reaction kinetics fitting of quenching reaction. Condition: $[MB]_0 = 25$ mg/L, $n[PDS]_0 : n[Sodium\ sulfate] : n[MB]_0 = 50 : 50 : 1$, $[EtOH]_0 = 7.85$ g/L, $[TBA]_0 = 7.9$ g/L, $[p\text{-benzoquinone}]_0 = 1.0$ g/L, initial pH = 5.8 and temperature = 25 ± 2 °C.

cationic dyes.



MB decolorization by PDS with or without catalyst addition

From the above results, PDS can effectively decolorize MB, but the decolorization rate did exceed 70%. To verify whether the PDS dosage or the oxidative capability is enough for MB decolorization, the same amount of PDS was added after 20 minutes of reaction, and then FeSO_4 was added after 30 minutes of the reaction to observe further decolorization of MB. As shown in Figure 5, the MB decolorization rate showed little increase after adding the same amount of PDS for the second time, indicating that PDS dosage was not the main reason for the incomplete MB decolorization. Fe^{2+} can catalytically activate PDS to produce $\text{SO}_4^{\cdot-}$ as Equation (3) (Zhang *et al.* 2013), and then decolorize MB efficiently. After adding Fe^{2+} , the decolorization rate increased rapidly from 73.7 to 92.2% (Figure 5). The above results also suggested that PDS without external activator cannot completely decolorize MB through direct oxidation.

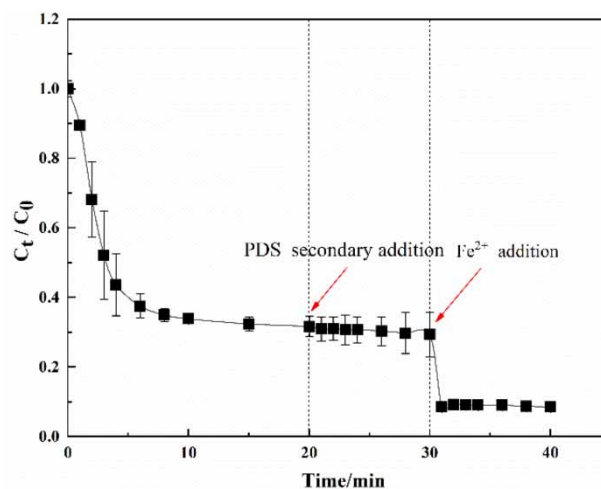
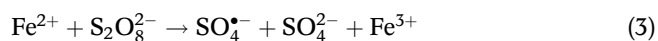


Figure 5 | MB decolorization by PDS with or without catalyst addition. Condition: $[MB]_0 = 25$ mg/L, $n[PDS]_0 : n[MB]_0 = 50 : 1$, $n[PDS]_1$ (or $n[\text{Fe}^{2+}]_0$) : $n[MB]_0 = 50 : 1$, initial pH = 5.8 and temperature = 25 ± 2 °C.

UV-VIS spectrum and TOC for MB removal by PDS

UV-VIS spectrum and TOC analysis of MB solution were performed to further investigate the oxidative removal of MB by PDS via direct oxidation or radical oxidation, respectively, without or with FeSO_4 addition. As shown in Figure 6(a)–6(c), significant decrease of UV-VIS absorbance for MB and RhB was observed, but only limited decrease for OrgII was present in treatments by PDS without FeSO_4 addition. Moreover, the UV-Vis spectra for MB, RhB, and OrgII in treatments with FeSO_4 addition showed much

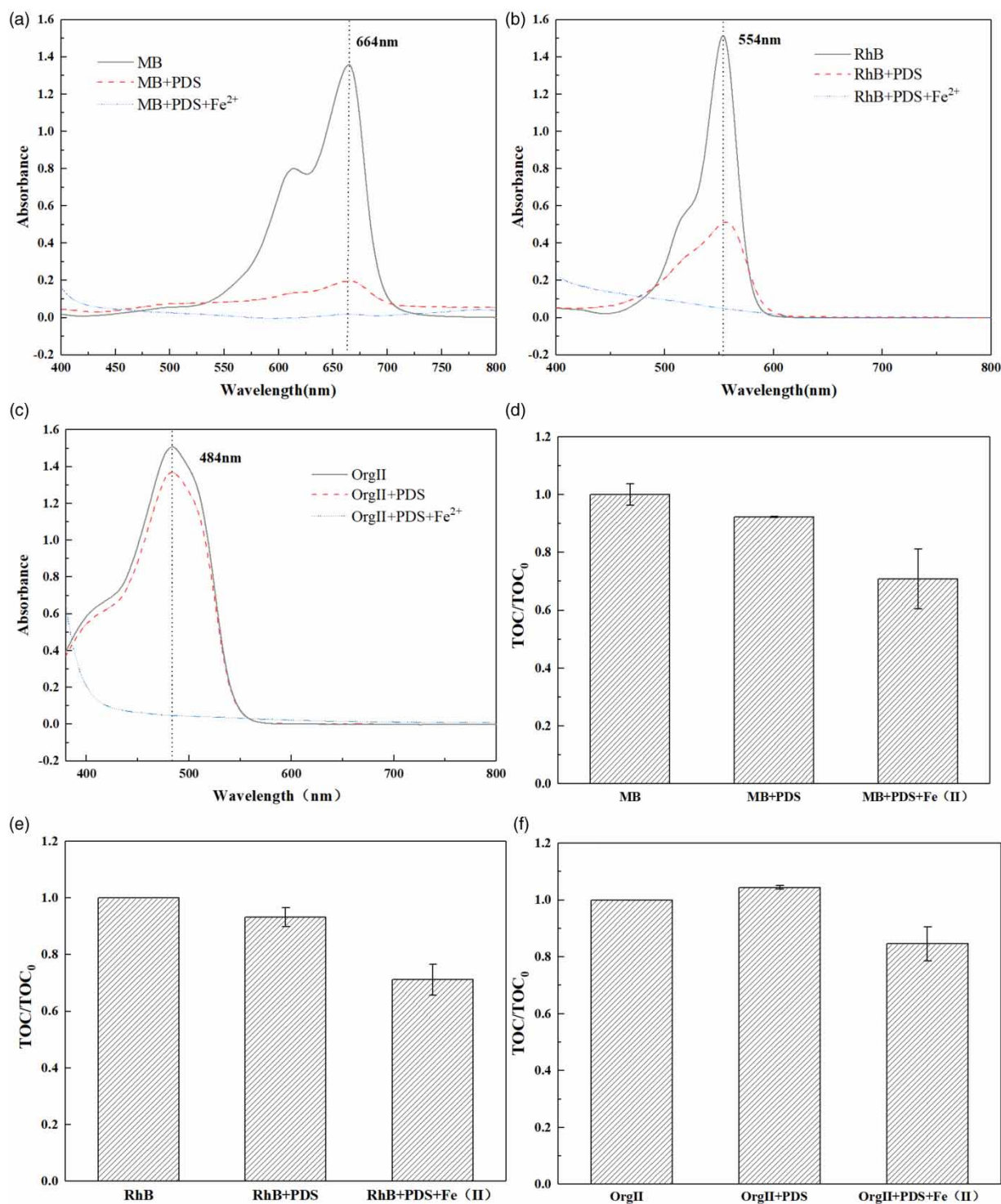


Figure 6 | UV-VIS spectra of (a) MB, (b) RhB, and (c) OrgII under different treatments. TOC removal of (d) MB, (e) RhB, and (f) OrgII under different treatments. Conditions: [MB]₀ = 25 mg/L, [RhB]₀ = 20 mg/L, [OrgII]₀ = 35 mg/L, n[PDS]₀: n[Fe²⁺]₀: n[MB]₀ (n[RhB]₀, or n[OrgII]₀) = 50:50:1, initial pH = 5.8 and temperature = 25 ± 2 °C.

less absorbance from 400 to 800 nm than those without FeSO₄ addition. In Figure 6(d)–6(f), dye removal rates in treatments by PDS without FeSO₄ addition were 7.7% and

6.8%, respectively, for MB and RhB, and showed almost no removal for OrgII. However, dye removal rates in treatments by PDS with FeSO₄ addition were significantly

increased to 29.1%, 28.8%, and 15.4%, respectively, for MB, RhB, and OrgII. In summary, the PDS can selectively and effectively decolorize MB and RhB by direct oxidation, but the removal rates of dyes were limited.

CONCLUSIONS

This study demonstrates that PDS without activation could effectively but selectively decolorize organic dyes, which was related to the charged states of dyes. Cationic dyes or dyes with positive charges under certain pH conditions were beneficial for the decolorization by PDS without activation. Thus, the researchers must pay attention to the contribution of PDS without activation to organic compound degradation, while studying the activation performance of various catalysts towards PDS to remove the selected model organic pollutants, especially when pollutants may carry positive charges under experimental condition. Direct and non-radical oxidation was proposed for the dye decolorization by PDS without activation. Compared with free radical oxidation via PDS with Fe^{2+} addition, direct decolorization of dyes by PDS without activation was not complete, and the degradation of dyes was limited. The applications of PDS direct oxidation on cationic dyes decolorization as emergency treatment could be possible, and further investigation about efficient decolorization and degradation of dyes should be warranted.

ACKNOWLEDGEMENTS

This study was partially supported by the National Natural Science Foundation of China (No. 21707111, 51808468) and Sichuan Science and Technology Support Project (No. 2020JDTD0018, 2019YJ0302).

AUTHOR DISCLOSURE STATEMENT

No competing financial interests exist.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Antonopoulou, M. & Konstantinou, I. 2014 Photocatalytic treatment of metribuzin herbicide over TiO_2 aqueous suspensions: removal efficiency, identification of transformation products, reaction pathways and ecotoxicity evaluation. *Journal of Photochemistry and Photobiology A Chemistry* **294**, 110–120.
- Clifton, C. L. & Huie, R. E. 1989 Rate constants for hydrogen abstraction reactions of the sulfate radical, SO_4^- . Alcohols. *International Journal of Chemical Kinetics* **21** (8), 677–687.
- Deister, U. & Warneck, P. 1990 Photooxidation of sulfite (SO_3^{2-}) in aqueous solution. *The Journal of Physical Chemistry* **94** (5), 2191–2198.
- Duan, X., Sun, H., Shao, Z. & Wang, S. 2018a Nonradical reactions in environmental remediation processes: uncertainty and challenges. *Applied Catalysis B: Environmental* **224**, 973–982.
- Duan, X., Sun, H., Tade, M. & Wang, S. 2018b Metal-free activation of persulfate by cubic mesoporous carbons for catalytic oxidation via radical and nonradical processes. *Catalysis Today* **307**, 140–146.
- Gao, W., Zhao, S., Wu, H., Deligeer, W. & Asuha, S. 2016 Direct acid activation of kaolinite and its effects on the adsorption of methylene blue. *Applied Clay Science* **126**, 98–106.
- Gao, Y. Q., Gao, N. Y., Chu, W. H., Zhang, Y. F., Zhang, J. & Yin, D. Q. 2019 UV-activated persulfate oxidation of sulfamethoxypyridazine: kinetics, degradation pathways and impact on DBP formation during subsequent chlorination. *Chemical Engineering Journal* **370**, 706–715.
- Jiang, X. X., Wu, Y. L., Wang, P., Li, H. J. & Dong, W. B. 2013 Degradation of bisphenol A in aqueous solution by persulfate activated with ferrous ion. *Environmental Science and Pollution Research* **20** (7), 4947–4953.
- Jiang, L., Zhang, Y., Zhou, M., Liang, L. & Li, K. 2018 Oxidation of Rhodamine B by persulfate activated with porous carbon aerogel through a non-radical mechanism. *Journal of Hazardous Materials* **358**, 53–61.
- Lee, H., Lee, H. J., Jeong, J., Lee, J., Park, N. B. & Lee, C. 2015 Activation of persulfates by carbon nanotubes: oxidation of organic compounds by nonradical mechanism. *Chemical Engineering Journal* **266**, 28–33.
- Lei, Y., Chen, C. S., Ai, J., Lin, H., Huang, Y. H. & Zhang, H. 2016 Selective decolorization of cationic dyes by peroxymonosulfate: non-radical mechanism and effect of chloride. *RSC Advances* **6** (2), 866–871.
- Li, D., Chen, D., Yao, Y., Lin, J., Gong, F., Wang, L., Luo, L., Huang, Z. & Zhang, L. 2016 Strong enhancement of dye removal through addition of sulfite to persulfate activated by a supported ferric citrate catalyst. *Chemical Engineering Journal* **288**, 806–812.
- Motohashi, N. & Saito, Y. 1993 Competitive measurement of rate constants for hydroxyl radical reactions using radiolytic hydroxylation of benzoate. *Chemical and Pharmaceutical Bulletin* **41** (10), 1842–1845.
- Neta, P., Huie, R. E. & Ross, A. B. 1988 Rate constants for reactions of inorganic radicals in aqueous solution. *Journal of Physical and Chemical Reference Data* **17** (3), 1027–1284.

- Ruiz, M., Yang, Y., Lochbaum, C. A., Delafield, D. G. & Pedersen, J. A. 2019 Peroxymonosulfate oxidizes amino acids in water without activation. *Environmental Science and Technology* **53** (18), 10845–10854.
- Shih, Y. J., Li, Y. C. & Huang, Y. H. 2013 Application of UV/persulfate oxidation process for mineralization of 2,2,3,3-tetrafluoro-1-propanol. *Journal of the Taiwan Institute of Chemical Engineers* **44** (2), 287–290.
- Song, X., Wang, C., Liu, M. & Zhang, M. 2018 Advanced treatment of biologically treated coking wastewater by persulfate oxidation with magnetic activated carbon composite as a catalyst. *Water Science and Technology* **77** (7), 1891–1898.
- Sun, D. D., Zheng, H. & Xue, W. P. 2012 Oxidation of phenol by persulfate activated with UV-light and Ag^+ . *Advanced Materials Research* **610–613**, 1806–1809.
- Swain, M. 2012 chemicalize.org. *Journal of Chemical Information and Modeling* **52** (2), 613–615.
- Tan, C., Gao, N., Deng, Y., An, N. & Deng, J. 2012 Heat-activated persulfate oxidation of diuron in water. *Chemical Engineering Journal* **203**, 294–300.
- Vinuth, M., Naik, H. S. B., Vinoda, B. M., Gururaj, H., Thomas, N. & Arunkumar, G. 2017 Enhanced removal of methylene blue dye in aqueous solution using eco-friendly Fe(III)-montmorillonite. *Materials Today-Proceedings* **4** (2), 424–433.
- Waclawek, S., Lutze, H. V., Grubel, K., Padil, V. V. T., Cernik, M. & Dionysiou, D. D. 2017 Chemistry of persulfates in water and wastewater treatment: a review. *Chemical Engineering Journal* **330**, 44–62.
- Wang, S. & Zhu, Z. H. 2007 Effects of acidic treatment of activated carbons on dye adsorption. *Dyes and Pigments* **75** (2), 306–314.
- Wang, S., Wu, J., Lu, X., Xu, W., Gong, Q., Ding, J., Dan, B. & Xie, P. 2019 Removal of acetaminophen in the Fe^{2+} /persulfate system: kinetic model and degradation pathways. *Chemical Engineering Journal* **358**, 1091–1100.
- Xu, Y., Ai, J. & Zhang, H. 2016 The mechanism of degradation of bisphenol A using the magnetically separable CuFe_2O_4 /peroxymonosulfate heterogeneous oxidation process. *Journal of Hazardous Materials* **309**, 87–96.
- Yang, S., Wang, P., Yang, X., Shan, L., Zhang, W., Shao, X. & Niu, R. 2010 Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: persulfate, peroxymonosulfate and hydrogen peroxide. *Journal of Hazardous Materials* **179** (1–3), 552–558.
- Yang, Y., Banerjee, G., Brudvig, G. W., Kim, J. H. & Pignatello, J. J. 2018 Oxidation of organic compounds in water by unactivated peroxymonosulfate. *Environmental Science and Technology* **52** (10), 5911–5919.
- Yu, J., Tang, L., Pang, Y., Zeng, G., Wang, J., Deng, Y., Liu, Y., Feng, H., Chen, S. & Ren, X. 2019 Magnetic nitrogen-doped sludge-derived biochar catalysts for persulfate activation: internal electron transfer mechanism. *Chemical Engineering Journal* **364**, 146–159.
- Zarei, A. A., Tavassoli, P. & Bazrafshan, E. 2018 Evaluation of UV/ S_2O_8 process efficiency for removal of metronidazole (MNZ) from aqueous solutions. *Water Science and Technology* **2017** (1), 126–133.
- Zhang, T., Zhu, H. & Croue, J. P. 2013 Production of sulfate radical from peroxymonosulfate induced by a magnetically separable CuFe_2O_4 spinel in water: efficiency, stability, and mechanism. *Environmental Science and Technology* **47** (6), 2784–2791.
- Zhang, T., Chen, Y., Wang, Y., Roux, J. L., Yang, Y. & Croue, J. P. 2014 Efficient peroxydisulfate activation process not relying on sulfate radical generation for water pollutant degradation. *Environmental Science and Technology* **48** (10), 5868–5875.
- Zhou, Z., Liu, X., Sun, K., Lin, C., Ma, J., He, M. & Ou, Y. W. 2019 Persulfate-based advanced oxidation processes (AOPs) for organic-contaminated soil remediation: a review. *Chemical Engineering Journal* **372**, 836–851.
- Zhu, S., Li, X., Kang, J., Duan, X. & Wang, S. 2019 Persulfate activation on crystallographic manganese oxides: mechanism of singlet oxygen evolution for nonradical selective degradation of aqueous contaminants. *Environmental Science and Technology* **53** (1), 307–315.

First received 1 March 2021; accepted in revised form 23 April 2021. Available online 6 May 2021